Asian Journal of Chemistry Vol. 5, No. 4 (1993), 979–983

Extension of Flory Theory to Some Simple Fluids at Elevated Temperature

M.C. SAXENA
Chemistry Department, K.S. Saket (P.G.) College
Faizabad-224 001, India

Sound velocity in some simple fluids argon, nitrogen, and oxygen has been evaluated over a wide range of temperature using Flory's statistical theory. The calculated values are compared with sound velocity obtained on the basis of hard sphere model and perturbation theory. The present values were found to be superior over the others.

INTRODUCTION

Successful attempts have been made by several investigators for the evaluation of sound velocity in molecular liquids and liquid mixtures from Flory's statistical theory[1–3] using Auerbach's relation[4]. A number of workers[5–9] have extended Flory's statistical theory for the evaluation of surface tension and sound velocity in case of liquids metals, molten salts and molten salt mixtures respectively. Pandey[10–12] and Misra[13] have also extended Flory's theory of the evaluation of sound velocity in pure molecular liquids at elevated pressures. Recently Pandey *et al*[14] have also successfully calculated the surface tension and sound velocity of Pb–Sn alloys using the Flory's theory. It appears from the literature that no attempts has so far been made for the evaluation of sound velocity in fluids over a wide range of temperature using Flory's theory. Although Purkait and Majumdar[15] calculated the sound velocity in fluids over a wide range of temperature using Perturbation theory and compared the results with the experimental values. In the present paper, we have evaluated here the sound velocity in liquid fluids. Ar, N_2 and O_2 over a wide range of temperature in the light of Flory's theory.

Theoretical

According to Auerbach's[4] relation, the velocity of sound U_1 is expressed by the relation

$$U_1 = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho}\right)^{2/3} \quad (1)$$

where σ and ρ are the surface tension and density respectively. According to Flory's theory the surface tension, σ is given by

For correspondence: Madhuban, 368-F, Balla Hata, opp. Sona Biscuit Co. Hospital Road, Faizabad-224 001, India

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{V}) \tag{2}$$

where σ^* and $\tilde{\sigma}(\tilde{V})$ are the characteristic surface tension and reduced surface tension respectively. The characteristic surface tension as given by Patterson and Rostogi[16] in their extension of corresponding state theory[17,18] can be expressed as

$$\sigma^* = k^{1/3} p^{*2/3} T^{*1/3} \tag{3}$$

Here k is the Boltzmann constant, P^* the characteristic pressure and T^* is the characteristic temperature. Starting with the work of Prigogine and Saraga[17] and using Flory's model of the liquid state, they also derived a reduced surface tension equation[16]

$$\tilde{\sigma}(\tilde{V}) = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2} \ln \frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1} \tag{4}$$

where $\tilde{V}$ is the reduced volume and M is the factional decrease in the neighbourhood of a cell in the surface phase as compared to the bulk phase. Its most suitable[19,20] value is 0.29. Pandey[10-11] and Mishra[13] have suggested some modification to its previous values in order to obtain better results at the elevated pressure. Recently Pandey *et al*[5-7] and Chaturvedi *et al*[6] used an alternative value in the case of molten salts and liquid metals. This value differs from those used for molecular liquids and liquid mixtures. In the present paper, we have used 0.42 for M. The characteristic temperature and pressure were computed by using the reduced equation of state as given by Flory, which is assumed to hold universally but which avoids the urealistic parameter of intermolecular energy as stipulated by theorem of corresponding state

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}} \tag{5}$$

$\tilde{P}$ and $\tilde{T}$ stands for the reduced pressure and reduced temperature respectively and are expressed by equation

$$\tilde{P} = \frac{P}{P^*}, \tilde{T} = \frac{T}{T^*} \text{ and } \tilde{V} = \frac{V}{V^*} \tag{6}$$

Equations (3) and (4) have been derived in the light of reduced equation of state[1-3]

$$\tilde{V} = \left[\frac{\alpha T}{3 + 3\alpha T} + 1\right]^3 \tag{7}$$

$$\tilde{P} = \frac{\alpha T \tilde{V}^2}{\beta_T} \tag{8}$$

and

$$T^* = \frac{T\tilde{V}^{4/3}}{\tilde{V}^{1/3} - 1} \tag{9}$$

where α and β_T are respectively the thermal expension coefficient isothermal compressibility.

RESULTS AND DISCUSSION

The computed values of sound velocity using Flory's theory vide equation (1) of simple fluids Ar, N_2 and O_2 over a wide range of temperature are listed in column six of Table-1, whereas the experimental[11] value of U are shown in column seventh. The experimental[13] values of thermal expansion coefficient isothermal compressibility and other essential data for the evaluation of sound velocity, were taken from the literature[15,22]. The computed values of reduced surface tension and surface tension using equation (4) and (2) are listed in column fourth and fifth respectively.

TABLE 1
SOUND VELOCITY OF SIMPLE FLUIDS ARGON, NITROGEN AND OXYGEN AT DIFFERENT TEMPERATURE

Fluid	Temperature K	$\tilde{V}$	$\tilde{\sigma}\tilde{V}$	σ dyne/cm	U cal m/sec.	U exp. m/sec.	Δ% error
Argon	84	1.2975	0.0869	22.75	856.9	860.2	0.4
	86	1.3042	0.0852	22.27	850.2	846.8	0.4
	87	1.3080	0.0843	22.04	847.0	840.0	0.8
	88	1.3119	0.0834	21.81	843.8	833.1	1.3
	89	1.3157	0.0824	21.59	840.8	826.4	1.7
	87.29*	1.3091	0.0841	22.09	849.3	—	—
Nitrogen	65	1.2718	0.0931	19.46	1075.2	875.0	9.3
	70	1.2975	0.0869	17.83	1032.1	923.5	10.5
	75	1.3209	0.0812	16.68	1004.9	873.0	13.1
	80	1.3442	0.0761	15.71	983.4	822.0	16.4
	85	1.3684	0.0712	15.01	972.0	772.0	20.6
	90	1.3928	0.0668	14.39	863.6	721.0	25.2
	77.2*	1.3314	0.0788	16.11	989.8	—	—
Oxygen	65	1.2057	0.1163	27.67	1055.2	1104.5	4.7
	70	1.2217	0.1102	26.84	1047.5	1066.0	1.8
	80	1.2539	0.0982	25.21	1031.8	988.0	4.2
	90	1.2559	0.0900	24.14	1030.6	909.0	11.8
	90.13*	1.2862	0.0899	24.07	1028.9	—	—

*Boiling point of the liquid.

It is clear from the Table that the calculated values of sound velocity are always decreasing similar to the experimental values, with increase of temperature.

Although equation (1) is empirical in nature, its validity is well justified[23], as it gives a maximum error of ± 4% for theoretical sound velocity results, if all the

experimental data are precise. Since in the present case the experimental values of surface tension of these fluids over a wide range of temperature , are not available in literature only a compansion of the experimenal sound velocity with those predicted theoretical is possible.

The percentage deviation between theoretical and experimental values are given in the eight column of the Table-1. An inspection of the last three percentage deviation between theoretical and experimental values lies between 0.4 to 25.2 with an average of 7.8. Thus agreement between the theoretical and experimental values is satisfactory. Purkait *et al*[15] computed the values of sound velocity U of argon, nitrogen and oxygen over a wide range of temperature using perturbation theory and hard sphere model. The average percentage deviations of their results based on these theory from the experimental values are 29.1 and 37.2 respectively. Therefore, it is clear from the Table-1 that Flory's theory gives better agreement with experimental values of sound velocity in comparison with other theoretical[15] values. One may therefore conclude that Flory's statistical theory can also be applied in the case of liquid fluids over a wide range of temperature.

ACKNOWLEDGEMENTS

The authors are grateful to Sri Y.R. Tripathi, Principal, and Dr. M.P. Gupta, Head of Chemistry Department, Saket Post Graduate College, Faizabad for providing library facilities during the work.

REFERENCES

1. P.J. Flory, R.A. Oswole and A.J. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).
2. P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
3. A. Abe and P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1838 (1965).
4. H. Auerbach, *Experimentia*, **4**, 473 (1948).
5. R.P. Pandey and B.R. Chaturvedi, *Chem. Scripta*, **18**, 65 (1981).
6. B.R. Chaturvedi, R.P. Pandey and J.D. Pandey, *J. Chem. Soc. Faraday, Trans. I*, **78**, 1039 (1982).
7. J.D. Pandey, B.R. Chaturvedi and R.P. Pandey, *J. Phys. Chem.* **85**, 1750 (1981).
8. J.D. Pandey and V. Gupta, *J. Phys. Chem.*, **86**, 5234 (1982).
9. J.D. Pandey and Alec. D.M. David, *J. Chem. Phys.*, **77**, 1064 (1982).
10. J.D. Pandey, *J. Chem. Soc. Faraday Trans. I*, **76**, 1215 (1980).
11. _____, *J. Chem. Soc. Faraday, Trans. I*, **75**, 2160 (1979).
12. J.D. Pandey and H. Pant, *J. Am. Chem. Soc.*, **104**, 3299 (1982).
13. R.L. Misra, *J. Chem. Phys.*, **73**, 5301 (1980).
14. R.P. Pandey and J.D. Pandey, *J. Phys. Chem. Liquids*, **14**, 253 (1985).
15. Asim R. Purkait and D.K. Majumdar, *Indian J. Pure and Appl. Phys.*, **17**, 222 (1979).

16. D. Patterson and A.K. Rastogi, *J. Phys. Chem.*, **74**, 1067 (1970).
17. I. Prigogine and L. Sarga, *J. Chem. Phys.*, **49**, 399 (1952).
18. R. Defay, I, Prigogine, A. Belemans and D.H. Ever, Surface Tension and Adsorption, Chap. XI, Longmans, London (1966).
19. D. Patterson, S.H. Bhattacharya and P. Pickes, *Trans. Faraday Soc.*, **64**, 648 (1968).
20. M.D. Croucher and M.L. Hair, *J. Phys. Chem.*, **81**, 1631 (1971).
21. W. Van Dael, A. Van. Itterbeak, A. Capsans, *J. Toem. Physica*, **32**, 611 (1966).
22. S. Yosam, *J. Chem. Phys.*, **40**, 3069 (1964).
23. R.L. Mishra, D. Phil. Thesis (University of Allahabad), 1977.

(*Received*: 1 June 1992; *Accepted*: 18 February 1993) AJC-562.